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Abstract

Rapid growth of smart electronics and implantable medical devices markets has driven the development of next-generation sustainable, flexible, or implantable batteries. Conducting polymers with unique mechanical and electronic properties offer new possibilities and have attracted great attention. In this review, we discuss approaches used to tune conducting polymers at the molecular level for designated properties and applications such as improved electrochemical performance, and we discuss approaches used to tune conducting polymers at the molecular level to enhance selected properties for applications such as lithium/sodium ion batteries, biodegradable electrodes or enhanced solution processability for advanced manufacture of such structures. We provide here insights into the molecular structure-electrochemical performance relationships. Finally, we present perspectives on the further development of conducting polymer materials for these novel batteries.

Disciplines

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Tunable Conducting Polymers: Toward Sustainable and Versatile Batteries

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Abstract

Rapid growth of smart electronics and implantable medical devices markets have driven the development of next generation sustainable, flexible, or implantable batteries. Conducting polymers with unique mechanical and electronic properties offer new possibilities and have attracted great attention. In this review, we discuss the main approaches used to tune conducting polymers at molecular level for designated properties and applications such as improved electrochemical performance, we discuss approaches used to tune conducting polymers at the molecular level to enhance selected properties for applications such as lithium/sodium ion batteries, biodegradable electrodes or enhanced solution processability for advanced manufacture of such structures. We provide here insights into the molecular structure-electrochemical performance relationships. At last we present perspectives on the further development of conducting polymer materials for these novel batteries.

Keywords: Conducting polymers, batteries, electrodes, doping, structure-property relationships.

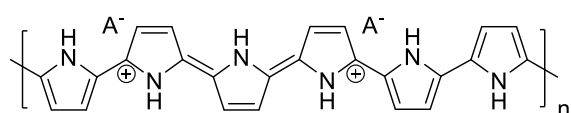
Introduction

Energy storage is the cornerstone of a sustainable energy supply system. It bridges the gap between the intermittent energy generated from renewable power sources such as solar, wind, and high energy on demand. Portable electronic devices such as laptops, smartphones,

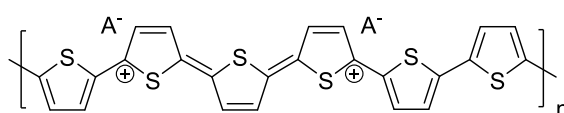
integrated circuit smart cards and wearable sensors have become an integral part of daily life.¹ ² The performance of these devices is critically dependent on the energy supply system, which is currently dominated by lithium and lithium-ion batteries (LIBs); owing to their high energy density, long service life and wide operating temperature in comparison to other energy storage systems.^{3,4} Inorganic materials (mainly transition metal compounds) have been widely used as cathode materials since the commercialisation of LIBs in 1991 by Sony.⁵ Great concern has arisen with the large-scale use of transition metal based electrode materials: sustainability of resources, environmental pollution and large energy consumption in both synthesis and recycling. The use of these non-renewable materials challenges the sustainable development of energy storage devices.⁶⁻⁹ Organic electrode materials can be considered as sustainable materials, as they may be extracted directly or eventually synthesized from biomass and recycled through carbon dioxide cycling.¹⁰ Ideally, there would be no additional CO₂ footprint in the whole process, and much less energy is consumed during chemosynthesis and thermal recycling. These organic electrodes may circumvent the drawbacks of resources depletion and environmental issues from using metal-based compounds electrodes.^{11, 12}

Currently there has also been a surge in demand for flexible and wearable electronics that can monitor, sense and communicate,^{13, 14} and this puts extra demands on power sources possessing similar configurations and functionalities. These ambitious requirements have triggered rapid developments in versatile electrode materials with flexibility, printability and new functionality. For some applications, cytocompatible and biodegradable structures would be ideal in providing transient functions to enhance biological processes, such as wound healing, bone revival or muscle repair.^{15, 16} Compared to the commonly used inorganic intercalation materials, electroactive organic materials with inherent redox properties are promising candidates. Organic electrode materials mainly include conducting polymers (CPs), organosulfur compounds, organic free radical compounds, and organic carbonyl compounds.^{17, 18} Amongst them, CPs are promising materials for sustainable and versatile batteries because of their unique electronic properties of metals or metal oxides and mechanical properties of polymers.¹⁹ Their high electrochemical performance in combination with unique features of flexibility, processability and structural diversity provide them great perspective in a variety of battery systems, such as lithium ion²⁰, sodium ion²¹, metal air²², lithium-sulfur²³ and all-polymer batteries²⁴.

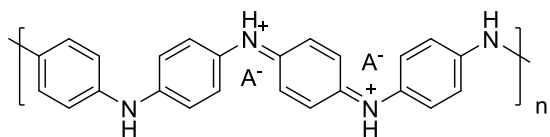
CPs are characterized by a polymer backbone consisting of alternating single and double bonds. Their overlapping p-orbitals create a system of delocalised π -electrons, leading to interesting and useful optical and electronic properties.²⁵ The most fascinating CPs for battery applications are polyheterocycles, such as polypyrrole (PPy), polyaniline (PANI), polythiophene (PTh), poly(3,4-ethylenedioxythiophene) (PEDOT) and their derivatives (molecular structures shown below).²⁶ They typically exhibit an electrical conductivity in the range of 0.01 to 500 S cm⁻¹.²⁷ The use of CPs in lithium batteries (*i.e.* PANI as cathode material) can be traced back to the late 1980s.^{28, 29} Research in this area is continuing to grow with the objective to tune their intrinsic properties. The great structural diversity and synthetic tailorability of CPs enable tuning of electrochemical properties (*i.e.*, redox potential, doping level, number of electrons involved) and/or introducing of new functionalities (*i.e.*, solution processability, biodegradability).^{30, 31}



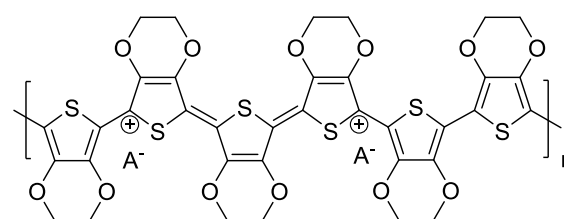
Polypyrrole (PPy)



Polythiophene (PTh)



Polyaniline (PANI)



Poly(3,4-ethylenedioxythiophene) (PEDOT)

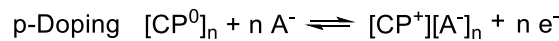
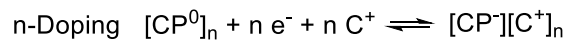
A number of excellent reviews have appeared that focus on the deployment of CPs in battery technology.³²⁻³⁵ However, no dedicated review about tuning CPs for targeted properties at molecular level is available, neither for the emerging type of implantable, spinnable and printable batteries. Here we provide a comprehensive review of CPs for the next-generation of sustainable and versatile batteries. It starts with a general introduction of the working principles and reaction mechanisms of well-established Li-ion batteries and relatively new Na-ion batteries. Modifying CPs with redox active groups to improve the electrochemical properties are critically discussed. Then their applications in new emerging cytocompatible/biodegradable batteries are discussed along with the introduction of additional functionalities. We also present the development of spinnable and printable CPs electrodes for batteries with unconventional

configurations through engineering their solution processability. Lastly, we provide perspectives for future development of CPs electrodes.

Conducting Polymers in Lithium Ion and Sodium Ion Batteries

Operation Principle

The electroactivity and conductivity of CPs facilitate their applications in rechargeable batteries. An extended π -conjugation endows CPs with metal-like or semiconductor properties. They are only conducting when doped, and the electrical conductivity depends on the extent of doping.^{36, 37} Doping is the process of reducing (n-doping) or oxidizing (p-doping) a neutral polymer through incorporation of a counter cation or anion (dopant), as illustrated in the following reactions where C^+ and A^- represents the doping counterions.³⁸



This process introduces charge carriers in the form of charged polarons (radical ions) or bipolarons (dications or dianions) into the polymer. During the doping/dedoping process, counterions are expelled from or migrate into the polymer backbone to maintain electroneutrality.³⁹

The fact that CPs can be charged/discharged is attributed to the doping/dedoping process accompanied with the mobility of anions or cations. CPs are commonly used as cathodes owing to their electrochemical stability in p-doped states. In a Li-ion battery, a p-type CP serves as the cathode and a carbon material functions as the anode (**Figure 1**). Dopants (A^-) are transferred from cathode to electrolyte, while Li ions are transferred from anode to electrolyte. Electrolyte should contain sufficient Li^+ and A^- to ensure conductivity and availability of ions. The discharge process involves the uptake of electrons and release of dopant anions for CP, while the anode gives up electrons and releases Li ions. During the charging process, Li cations are reduced and stored in the carbon material, while the CP is simultaneously oxidized by losing electrons.⁴⁰

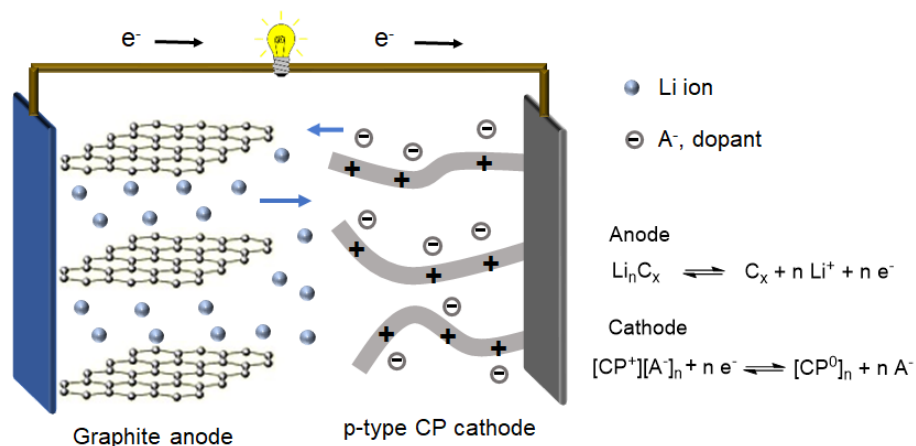


Figure 1 General redox chemistries and a schematic working principle of a Li-ion battery using a p-type CP cathode and a carbon-based anode during discharge; A^- represents the doping ions.

Sodium-ion batteries (SIBs) are emerging as an alternative to LIBs due to the abundance of Na in the earth's crust.⁴¹ Since Li and Na share common properties as alkali metals, the working principle of SIBs is similar to that of LIBs.⁴² However, research on SIBs is still in its infancy with the search for active materials with sufficiently large interstitial spacing to host Na ion. The Na ion has an ionic radius 0.3 Å larger than Li ion.⁴³ In terms of CPs, their “soft” nature allows the intercalation of ions in large size, thus they are suitable materials for SIBs as well.⁴⁴

Modification of Conducting Polymers

The specific capacity offered from CPs is attributed to their attainable doping levels.⁴⁵ CPs typically possess a doping level of 0.3-0.5 (*i.e.*, 0.5 holes per monomer ring in PANI, 0.33 in PPy and 0.25 in PTh),⁴⁶ affording a capacity in the range of 82-147 mAh g⁻¹.³² Higher doping levels may lead to irreversible destruction of CPs.⁴⁷ CPs suffer from another critical issue of sloping voltage profile when discharged, because the voltage of CPs strongly depends on the doping level and it changes upon charging/discharging.⁴⁸ These drawbacks may be overcome by using organic synthetic tools such as embedding redox active groups at molecular level. It can be achieved through either covalently linked to polymer backbone as pendants (forming conducting redox polymers) or doped into the polymer matrix as a counterion.⁴⁹ Organic redox molecules that can be incorporated into the CPs matrix mainly include metal complexes, carbonyls, radical compounds, and organosulfur compounds, which contain atoms with lone pair electrons such as N, S, and O.^{50, 51} This design facilitates the insertion/extraction of Li/Na ions in addition to the doping/dedoping process of CPs.^{52, 53} Thus, they can harness the properties of both the conjugated polymeric backbone (providing conducting path and charge

capacity) and redox groups (introducing additional charge capacity), thereby enhancing performance. It should be pointed out that the integration of organic redox molecules interrupts the π -conjugation of CPs and limits the ability to stabilize the charge carrier. Thus, the doping level of CPs is limited resulting in lower electronic conductivity..

Polypyrrole (PPy)

PPy consists of repeating units of pyrrole that are primarily connected at the α -positions. The additional functionality can be obtained by substitution on the available β -carbon or nitrogen. In 2007, Park *et al.* covalently anchored ferrocene groups on the nitrogen of pyrrole unit, yielding a copolymer with 50% functionalized unit (**Figure 2a**).⁵⁴ This redox pair presented its own charge storage behavior displaying flat charge/discharge plateau in contrast to the sloping one for PPy. The formed pyrrole/[(ferrocene) amidopropyl]pyrrole copolymer (PPy/ferrocene) displayed a specific capacity of 65 mAh g⁻¹, higher than that 20 mAh g⁻¹ for unmodified PPy (Figure 2b). Redox-active molecule viologen can be covalently bound with the pyrrole unit via an alkyl linker at the nitrogen position (PPy-V²⁺-Me, Figure 2c).⁵⁵ With three one-electron redox states, viologens exhibited rapid and reversible electron transfer at lower potential. This material exhibited a capacity of 55 mAh g⁻¹ when coupled with Li foil anode, higher than 30 mAh g⁻¹ from PPy incorporated with 1,1'-bis(2,4-benzenedisulfonate)-4,4'-bipyridinium dibromide (VTS) (PPy[VTS]) (Figure 2d). As an organic nitroxyl radical group, 2,2,6,6-tetramethylpiperidine-N-oxyl (TEMPO) reveals excellent electrochemical stability and fast redox kinetics.⁵⁶ Recently, it has been introduced as pendant substituents at the N position of pyrrole unit.⁵⁷ A significantly improved discharge capacity of 115 mAh g⁻¹ was achieved, compared with only 16.5 mAh g⁻¹ for pure PPy.

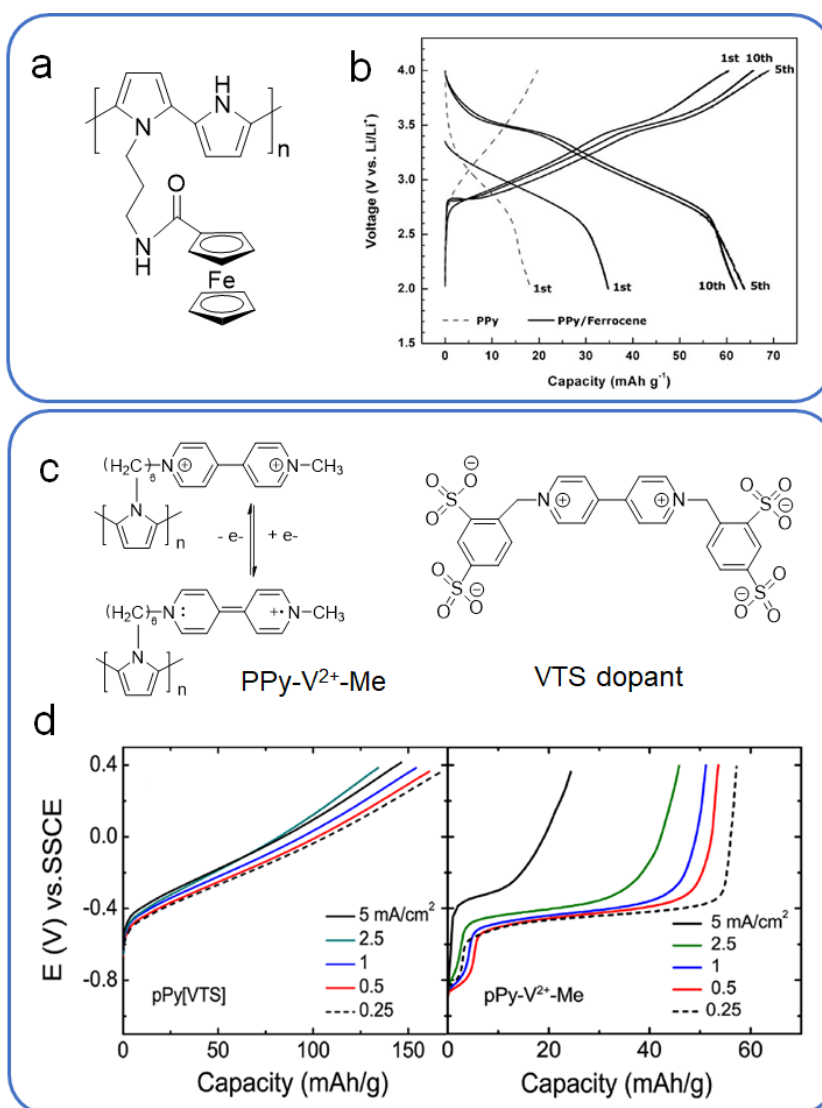


Figure 2 (a) Chemical structure of PPy/ferrocene; (b) Charge-discharge curves of PPy and PPy/ferrocene polymer cathode in a LIB at C/5; (Reproduced with permission from ref. 54. Copyright 2007, WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim). (c) Chemical structures of PPy with viologen as pendant substituent and PPy with [VTS] as dopant; (d) Discharge curves of PPy[VTS] and PPy-V²⁺-Me; (Reproduced with permission from ref. 55. Copyright 2013, American Chemical Society).

Substitution on nitrogen is relatively easy to achieve but has detrimental effects on the conductivity due to the steric hindrance from the twisted pyrrole units. Using β -substitution is a promising option to achieve functionalization without disrupting the PPy backbone. Sjödin's group has developed a series of CRPs based on PPy with hydroquinone pendant groups that are attached to the β -carbon via different linkers.^{58, 59} Quinone is a carbonyl compound with low molar mass molecular that undergoes a reversible two-electron exchange process at a

relatively high potential (~ 2.6 V vs. Li/Li⁺), affording a theoretical specific capacity of 495 mAh g⁻¹.⁶⁰ Organosulfides are another type of redox groups used to modify pyrrole unit at the β -position. They contain disulfide bonds providing the charge capacity through a S-S electro-dimerization/scission redox reaction.¹² An intramolecular cyclic disulfide-containing poly(4,6-dihydro-1H-[1,2]dithiino[4,5-c]pyrrole) showed less over-oxidation, good redox properties, and a high discharge capacity of 398 mAh g⁻¹ as a cathode material in lithium secondary batteries.⁶¹

In addition to covalently linking redox-active pendants into CPs backbones, another approach is to construct a Na host by grafting ionisable organic sodium salts on the polymer backbone.⁶² Na ions can be inserted/extracted from the polymer chain during the charge/discharge processes. The operational mechanism is insertion/extraction instead of conventional doping/de-doping. For example, Yang *et al.* developed a self-doped PPy by grafting nitrogen atom with ionizable sodium sulfonate.⁶³ Due to the immobile self-doping of organic anions, this material can act as a Na-host for reversible Na insertion-extraction reaction as evidenced by the distinct peaks in cyclic voltammograms (CV). The resultant poly(pyrrole-co-(sodium-3-(pyrrolyl) propanesulphonate)) copolymer (PPy-PS) was effective in storing Na ions and showed a capacity of 85 mA g⁻¹, and it was steady over 100 cycles.

Polyaniline (PANI)

In 1999, Hass *et al.* immobilized quinone groups into the benzoid of PANI backbone to improve conductivity and decrease solubility.⁶⁴ Quinone groups were first introduced to aniline monomer by the electropolymerization of naphthalene derivatives bearing -OH or -NH₂ groups as substituents. For example, 5-amino-1,4-naphthoquinone (ANQ) monomers are typically synthesised by nitrating 1,4-naphthoquinone in a mixture of concentrated H₂SO₄ and NaNO₃ at 5 °C, followed by the reduction into -NH₂ group by SnCl₂.⁶⁵ Polymers with a PANI-like structure are then chemically or electrochemically polymerized from the corresponding monomers. The resultant poly(5-amino-1,4-naphthoquinone) (PANQ) showed a capacity of about 290 mAh g⁻¹ with a discharge potential of 2.5-2.7 V vs. Li/Li⁺. Following this work, other types of CRPs with quinone connected to N-H group were developed.⁶⁶ A good capacity retention of 160 mAh g⁻¹ over 200 cycles was achieved for poly(1,5-diaminoanthraquinone) (PDAQ).⁶⁷ Recently, Vlad *et al.* reported on the synthesis of poly(2,5-dihydroxyaniline) (PDHA) by chemical demethylation with redox quinone as part of the polymer backbone (**Figure 3a**).⁶⁸ The intramolecular cross-hybridization of quinone redox and PANI moieties

lead to a subtle interplay between the redox stability and lithiation capacity, showing a theoretical capacity of 443 mA h g⁻¹. PDHA displayed a pair of redox peaks centred at 2.3 V and 2.6 V that could be assigned to a two-electron process for quinone groups (Figure 3b). The assembled cell coupled with lithium displayed an open circuit potential in a range of 2.8-3.2 V (vs. Li/Li⁺) (Figure 3c), and an initial capacity of 180 mAh g⁻¹ in an organic carbonate-based electrolyte.

Organosulfur polymers with disulfide bond in the main chain generally show a redox process accompanied by depolymerisation and structural changes of main chains.⁴⁸ The recombination efficiency of S-S bonds is very low leading to a poor reversibility.⁶⁹ It can be improved when the S-S bond is installed in the side chain. The first side chain type organosulfur polymer poly(2,2'-dithiodianiline) (PDTDA) was introduced as a cathode material in lithium batteries in 1997.⁷⁰ It had one S-S bond interconnected between two moieties of anilines. A capacity of 270 mAh g⁻¹ coupled with a flat voltage of 2.5 V vs. Li/Li⁺ was achieved using a gel polymer electrolyte. This PANI-based CRP showed a conductivity in the level of 10⁻² S cm⁻¹, two orders of magnitude lower than that 0.1-5 S cm⁻¹ for PANI;^{71, 72} as a result of the steric hindrance induced by the sulphide substitution for reduced structural order of polymers. Notably, a conducting PANI derivative containing -O-S-S-O- links, exhibited a high energy density (460 mWh g⁻¹).⁷³ In particular, the theoretical capacity of poly(α,α' -dithio-3-amino-o-xylene) (PDTAn) is 370 mAh g⁻¹ (assuming a doping level of 0.5 for PANI), higher than PDTDA thanks to the high sulfide density in the in-chain-disulfide design.⁷⁴

Other redox groups such as 2,2,6,6-tetramethylpiperidine-N-oxyl⁷⁵ and ferrocene unit⁷⁶ have also been introduced into the PANI backbone. A redox-active N-methylthionine unit was copolymerized with aniline monomer, yielding a copolymer (PANMTh) with phenothiazine ring in the main chain resulting in an improvement of electroactivity in high pH electrolyte.⁷⁷ When assembled in an aqueous Zn-polymer secondary battery, it delivered a high specific capacity of 146.3 mAh g⁻¹ and retained ~99.4% of the capacity over 150 consecutive cycles. Similar as Park's PPy work in 2007,⁵⁴ a copolymer ferrocene-substituted aniline was synthesized.⁷⁶ It demonstrated an improved discharge plateau over the potential range of 3.0-4.0 V (vs Li⁺/Li), and a good cycling stability with an 8% loss over 30 cycles.

Na-rich PANI cathode, poly(aniline-co-aminobenzenesulfonic sodium) (PANS), was recently developed by grafting electron withdrawing -SO₃Na groups onto PANI chains and investigated for SIB application (Figure 3d).⁷⁸ Due to the immobile dopant and effective activation of

sulfonate group, PANS cathode delivered a reversible capacity of 133 mAh g⁻¹ with an excellent capacity retention rate of 97% after 200 cycles (Figure 3e,f). It also showed an impressive rate capability possibly due to the flexibility of polymer framework affording less resistance to insertion/extraction of Na ions. Electron withdrawing o-nitroaniline had also been grafted onto PANI chains.^{79, 80} The aniline-nitroaniline copolymer P(AN-NA) delivered a capacity of 180 mAh g⁻¹ at an average potential of 3.2 V vs. Na/Na⁺ and a reversible capacity of 173 mAh g⁻¹ after 50 cycles.

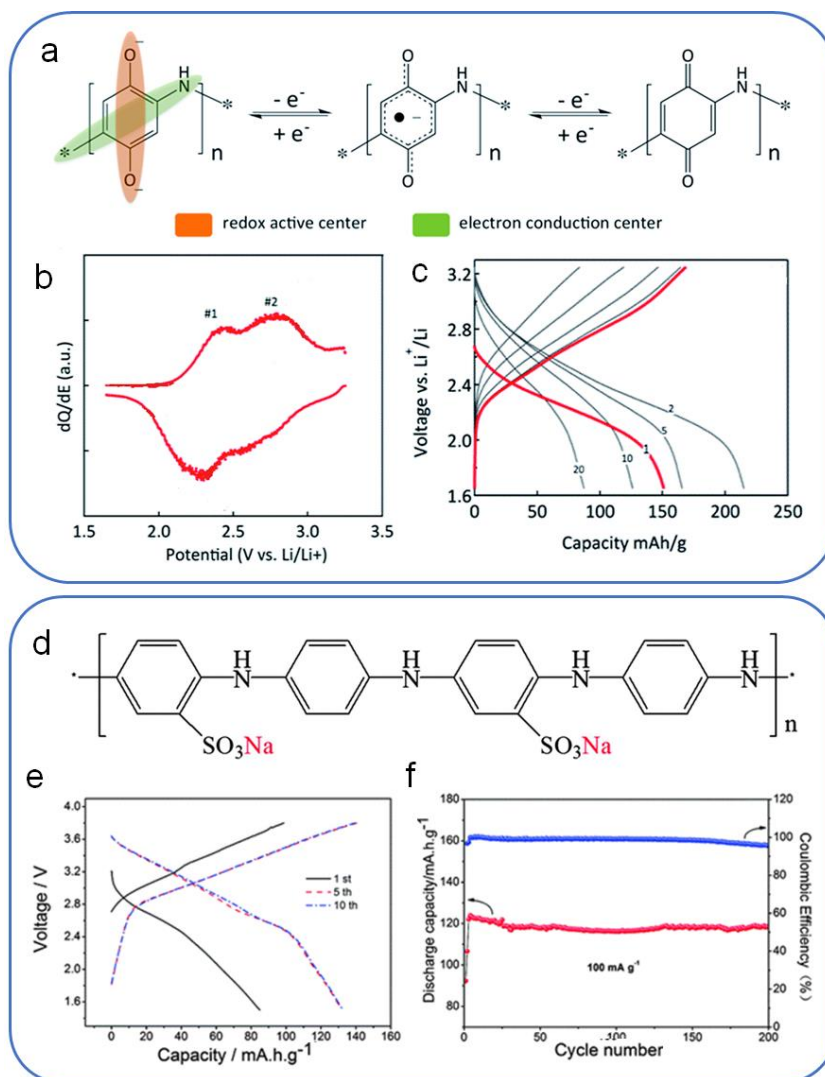


Figure 3 (a) Molecular formula and redox reactions of poly(2,5-dihydroxyaniline) (PDHA); (b) Differential capacity plots for PDHA, two characteristic redox peaks are related to a two-electron transfer for quinone groups; (c) Charge-discharge profiles (at C/10 rate) for PDHA; (Reproduced with permission from ref. 68. Copyright 2015, Royal Society of Chemistry). (d) The molecular structure of PANS; (e) Charge-discharge profiles during the first ten cycles at

50 mA g⁻¹; (f) Cycling performance at 100 mA g⁻¹. (Reproduced with permission from ref. 78. Copyright 2015, Royal Society of Chemistry).

Polythiophene (PTh)

PTh and its derivatives have attracted attention in the field of energy storage due to their stable n-doping state by using side chain functionalization.⁸¹ Like PPy, PTh can also be modified via grafting functional groups to β -carbon or sulfur atom. A stable anode β -substituted poly(phenylene-thiophene) material demonstrated a significant enhancement in the n-doping capacity.⁸² Introducing fluorine at the phenyl ring further improved the capacity and redox stability of poly(phenylene-thiophene).^{83, 84} The electron withdrawing effect from the substituent can stabilize the charge accumulation on the backbone, thereby increasing the doping level and stability. A series of fluorine-substituted poly(phenylene-thiophene) with fluorine atoms at various positions of phenyl ring have been designed and synthesized.⁸⁵ The electrochemical property of these functionalized CPs was influenced by the steric and electronic character of pendant groups. A maximum doping level of 0.45 holes per repeat unit was achieved coupled with a cycling efficiency of up to 99.58% attained per cycle.⁸³ The PTh incorporated with a high electron affinity group oxadiazole was endowed with a stable n-doping level of 1.35 per repeat unit in an ionic liquid electrolyte.⁸⁶

Recently, Liang *et al.* reported a conjugated redox polymer poly {[N,N'-bis(2-octyldodecyl)-1,4,5,8-naphthalenedicarboximide-2,6-diyl]-alt-5,5'-(2,2' bithiophene)} (P(NDI2OD-T2)) featuring stable and reversible n-doping with an enhanced electronic conductivity (**Figure 4a**).⁸⁷ This polymer was constructed by bridging a linear π -conjugated bithiophene unit, which provided an electron-transport pathway within a naphthalene dicarboximide (NDI) unit. Every NDI unit contained four carbonyl groups, two of which were expected to be reversibly reduced via a two-step two-lithium addition reaction corresponding to an n-doping level of ~ 2.0 . Being a Li storage material, P(NDI2OD-T2) delivered a specific capacity of 54.2 mAh g⁻¹, nearly 100% of its theoretical capacity (given a 2-electron redox reaction) (Figure 4b). It delivered 95% of its theoretical capacity at a high rate of 100C along with a 96% capacity retention rate over 3,000 cycles (Figure 4c). This ultrafast electrode kinetics was ascribed to high electronic conductivity at the heavily n-doped state. Another n-doping conjugated redox polymer with PTh backbone and diethyl terephthalate pendant groups was synthesized and applied as anode material in a LIB.⁸⁸ The conductivity of this polymer was not compromised by the presence of pendant groups, thus allowed for fast charge transport resulting in excellent rate capability.

Conjugated radical polymers have captured great attention for high power and fast redox kinetics.⁸⁹ However, they delivered very low specific capacity compared with their theoretical capacity.⁹⁰ Lutkenhaus *et al.* recently synthesized a series of β -substituted PTh bearing TEMPO radicals with varying alkyl spacer groups (Figure 4d).⁹¹ A specific capacity of 68 mAh g⁻¹ was delivered with tetramethyl alkyl groups, corresponding to 38.2% of its theoretical capacity. By monitoring the open circuit potential decay via *in situ* spectroelectrochemistry, a rapid dedoping process was verified for the PTh backbone, which was caused by internal electron transfer from the nitroxide group to PTh backbone (Figure 4e,f). This internal electron transfer interfered with the stabilization of polymer in the fully oxidized state.

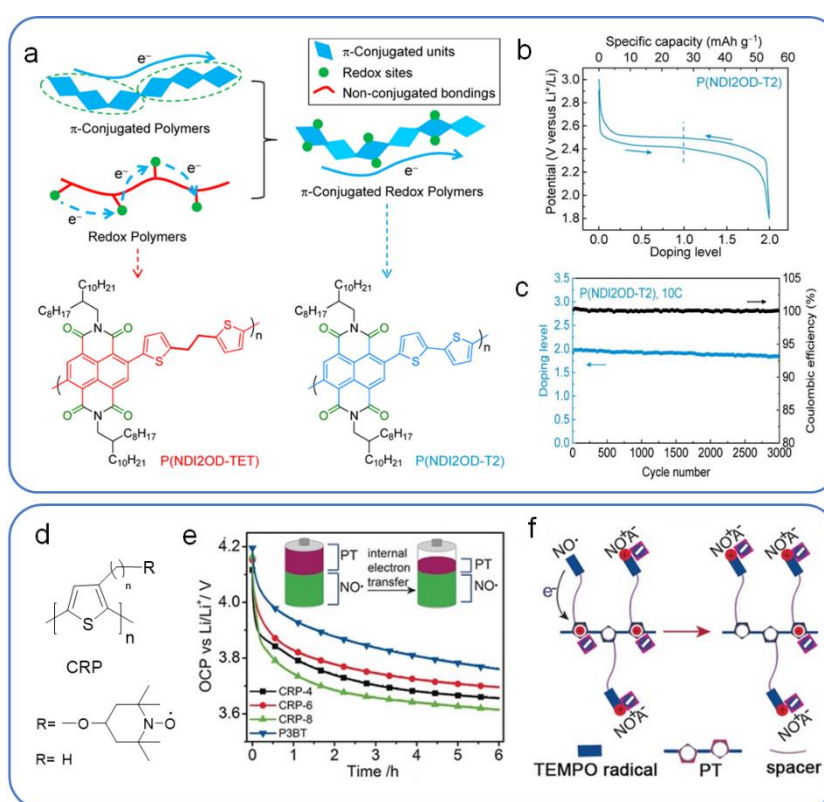
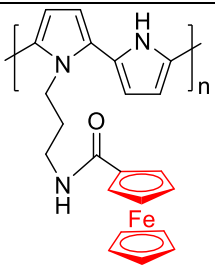
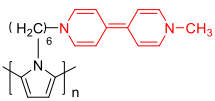
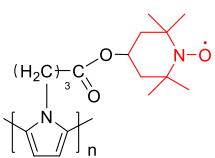


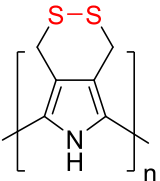
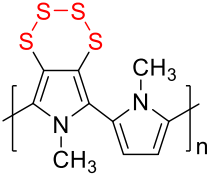
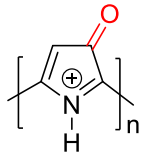
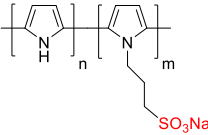
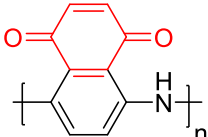
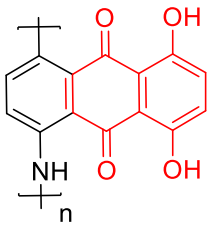
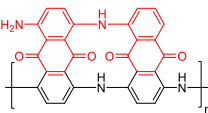
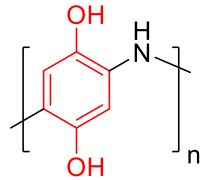
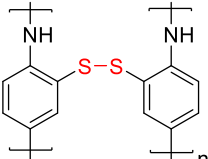
Figure 4 (a) Graphical illustration and molecular structure of non-conjugated P(NDI2OD-TET) and π -conjugated P(NDI2OD-T2); (b) Potential profile of P(NDI2OD-T2) during n-doping/dedoping at 1C; (c) Reversibility of P(NDI2OD-T2) during repeated n-doping/dedoping at 10C; (Reproduced with permission from ref. 87, Copyright 2015, American Chemical Society). (d) Chemical structure of PTh conjugated radical polymers with alkyl spacers; (e) Open-circuit potential monitoring for 6 h with an inset illustrating the changes of CRPs; (f) Illustration of an internal electron-transfer process occurring for CRP; (Reproduced with permission from ref. 91, Copyright 2017, WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim).

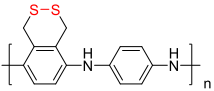
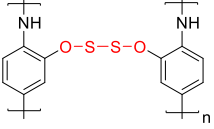
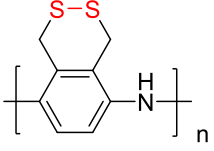
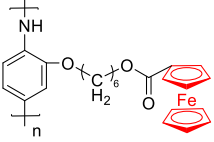
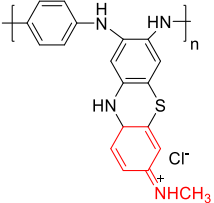
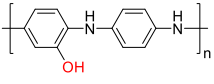
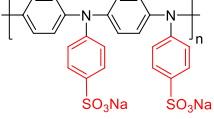
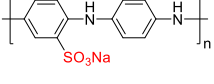
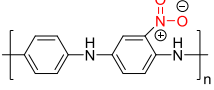
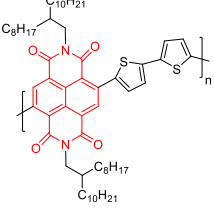
Vulcanization is a facile and low-cost method to stabilize polymeric sulfur against depolymerization. Recently, copolymers of PTh and sulfur prepared by the inverse vulcanization have demonstrated excellent electrochemical performance in Li-S batteries.^{92, 93} The poly(3-hexylthiophene-2,5-diyl) (P3HT) and S8 copolymer (S-P3HT) exhibits an enhanced battery performance with respect to the cycling performance at 0.5C (799 mAh g⁻¹ after 100 cycles for S-P3HTcopolymer versus only 544 mAh g⁻¹ for the simple mixture) and the C-rate performance.⁹⁴ This is attributed to the attractive interaction between polysulfides and P3HT hindering the dissolution of polysulfides and the charge transfer due to the homogeneous incorporation of P3HT into sulfur by covalently linking sulfur and P3HT.

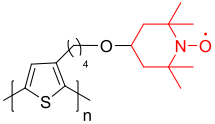
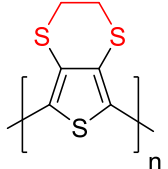
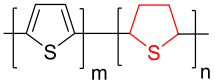
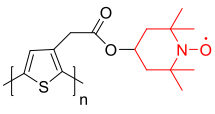
In this section, we have summarised the developments of CPs with redox-active groups and ionizable organic anions as electrode materials in secondary batteries. CRPs afford an improved battery performance in terms of higher plateau voltage, higher capacity and stable cyclic capability compared with pristine CPs. Further work should pay attention to the matching of redox potentials between redox groups and conjugated backbone for achieving a stable CRP. To provide an overview of this field, structures of conducting redox polymers and their performance are outlined in **Table 1** for a comprehensive comparison.

Table 1. Overview of conducting redox polymers in secondary batteries .

	Backbone	Structure*	Discharge Plateau (V)	Capacity (mAh/g)	Discharge current density	Capacity loss (cycle no.)	Ref.
Polypyrrole	poly pyrrole/[ferrocene amidopropyl]pyrrole (PPy/ferrocene)		3.5 vs Li/Li ⁺	65	0.2C	-	54
	poly(viologen pyrrole) (PPy-V ²⁺ -Me)		-	55	0.25 mA cm ⁻²	30% (100)	55
	poly(4-(3-(Pyrrol-1-yl) hexanoyloxy)-2,2,6,6-tetramethylpiperidin-		2.7 vs Li/Li ⁺	115	20 mA g ⁻¹	25% (50)	57

1-yloxy) (PPy-C-TEMPO)								
Polyaniline	poly(4,6-dihydro-1H-[1,2]dithiino[4,5-c]pyrrole) (Poly(MPY))		3.0 vs Li/Li ⁺	398	0.02C	93% (30)	61	
	poly(N-methylpyrrole) with pentathiepin rings (S-PMPy)		1.6-1.8 vs Li/Li ⁺	14.8	5 μA cm ⁻²	23% (8)	95	
	overoxidized PPy		1.5 vs Li/Li ⁺	284.9	1C	16% (1000)	96	
	poly(pyrrole-co-(sodium-3-(pyrrol-1yl)propanesulphonate)) (PPy-PS)		3.3 vs Na/Na ⁺	75	40 mA g ⁻¹	quite steady (100)	63	
	poly(5-amino-1,4-naphthoquinone) (PANQ)		2.5 vs Li/Li ⁺	290	0.07C	31% (17)	64	
	poly(5-amino-1,4-dihydroxyanthraquinone) (PADAQ)		-	322	400 mA g ⁻¹	58% (100)	66	
Polyaniline	poly(1,5-diaminoanthraquinone) (PDAQ)		2.2 vs Li/Li ⁺	285	20 mA g ⁻¹	57% (200)	67	
	poly(2,5-dihydroxyaniline) (PDHA)		-	180	0.1C	56% (20)	68	
	poly(2,2'-dithiodianiline) (PDTDA)		2.5 vs Li/Li ⁺	270	0.7 mA cm ⁻²	-	70	

	poly(5-amino-1,4-dihydrobenzo[d]-1,2-dithiadene-co-aniline) P(DTAn-co-An)		2.8 vs Li/Li ⁺	262	10 mA g ⁻¹	-	72
	poly[bis(2-aminophenyloxy)disulfide] (PAPOD)		2.0 vs Li/Li ⁺	230	0.1 mA cm ⁻²	70% (7)	73
	poly(α,α'-dithio-3-amino-o-xylene) (PDTAn)		2.6 vs Li/Li ⁺	225	10 mA g ⁻¹	-	74
	poly(aniline-co-6-(2-amino-phenol-9H-yl)-hexyl ferrocenecarboxylate) (PANFc)		3.4 vs Li/Li ⁺	88.2	20 mA g ⁻¹	24% (150)	75
	poly(aniline-co-N-methylthionine) (PANMTh)		1.2 vs Zn ²⁺ /Zn	146.3	1 mA g ⁻¹	0.6% (150)	77
	poly(aniline-co-m-aminophenol)		1.1 vs Zn ²⁺ /Zn	137.5	0.5 mA cm ⁻²	12% (120)	97
	poly(diphenylaminesulfonic acid sodium) (PDS)		3.4 vs Na/Na ⁺	30	50 mA g ⁻¹	30% (100)	62
	poly(aniline-co-aminobenzenesulfonic sodium) (PANS)		2.8-2.4 vs Na/Na ⁺	85	50 mA g ⁻¹	4% (200)	78
	poly(aniline/o-nitroaniline) P(AN-NA)		3.2 vs Na/Na ⁺	181	50 mA g ⁻¹	4% (50)	79
Polythiophene	poly{[N,N'-bis(2-octyldodecyl)-1,4,5,8-naphthalenedicarboximide-2,6-diyl]-alt-5,5'-(2,2'-bithiophene)} P(NDI2OD-T2)		-	47.4	1C	4% (3000)	87

poly(2, 2, 6, 6-tetramethyl-4-(4-(thiophen-3-yl)butoxy)piperidin-1-yloxy radical)		3.5-3.7 vs Li/Li ⁺	68	80 mA g ⁻¹	-	91
poly[3,4-(ethylenedithio)thiophene] (PEDTT)		2.2 vs Li/Li ⁺	425	50 mA g ⁻¹	17% (44)	98
polythiophene with thianthrene		2.2 vs Li/Li ⁺	400	50 mA g ⁻¹	49% (30)	99
poly(2,2,6,6-tetramethylpiperidin-1-oxyl-4-yl 2-(thiophen-3-yl)acetate)		3.6 vs Li/Li ⁺	79	0.05 mA	23% (50)	100

* Redox-active groups and ionizable organic anions grafted in the CPs are labelled in red.

Modification with Redox-Active Dopants

Modifying the backbone of CPs with redox-active functional groups can alleviate sluggish doping/de-doping process and improve charge storage capability. There still exists room to improve the performance by substituting those electrochemically inert dopants. For instance, the theoretical specific capacity of PPy/*p*-toluenesulfonate (*p*TS) (a 0.33 doping level, one electron transfer) is 133 mAh g⁻¹ if only taking pyrrole units into account, but it is down to 73 mAh g⁻¹ with the inclusion of dopant. Thus, using redox-active dopants instead is an effective way to improve charge storage by contributing additional capacity, and/or altering the redox mechanism of CPs. The prerequisite for choosing proper dopants is that their redox potential should fall into the operation voltage range of batteries, thus to facilitate electron transport and contribute their capacity.

Hexacyanoferrate is an important iron-containing redox-active species, which can afford a strong redox couple of Fe(CN)₆⁴⁻/Fe(CN)₆³⁻. Torres-Gomez *et al.* first doped PPy with potassium hexacyanoferrate (K₃Fe(CN)₆), and it displayed a specific capacity of 69 mAh g⁻¹ as a cathode for LIBs.¹⁰¹ Zhou and co-workers fabricated Fe(CN)₆⁴⁻-doped PPy cathodes.⁹¹ The Fe(CN)₆⁴⁻ ions served as a redox mediator to improve the charge transfer between polymer and electrolyte, as its redox potential (~ 3.0 V vs. Li/Li⁺) is close to the Fermi level of PPy (E_F =

+2.50 to +2.80V vs. Li/Li⁺).¹⁰² The resulting PPy/FC cathodes delivered a significantly improved specific capacity of ~145 mAh g⁻¹ in sharp contrast to that ~35 mAh g⁻¹ from undoped PPy over a high potential range of 1.5-4.0 V (vs. Li⁺/Li) at a current density of 50 mA g⁻¹. This material also exhibited great cycling stability with a capacity retention rate of 80% over 100 cycles at 50 mA g⁻¹. The Fe(CN)₆⁴⁻-doped PPy has demonstrated the application in NIBs as well, offering a high specific capacity of 135 mAh g⁻¹ at 50 mA g⁻¹ along with an excellent capacity retention rate of 85% over 100 cycles.¹⁰³

Deng *et al.* developed a redox-active molecule perylene-3,4,9,10-tetracarboxydiimide (PTCDI) doped PPy. It demonstrated an oxidation/reduction pair at +3.0/+2.0 V (vs. Li/Li⁺), which was derived from association/dissociation of Li⁺ to carbonyl groups.¹⁰⁴ PTCDI has low solubility in most organic electrolytes affording an improved long-term cycling stability. This material demonstrated a high reversible capacity of >100 mAh g⁻¹ at a current density of 50 mA g⁻¹, and a high capacity retention rate of 92% over 200 cycles. Diphenylamine-4-sulfonate (DS) displayed two reversible redox reactions in the Na⁺-containing electrolyte, 3.5-3.8 V and 3.3-3.6 V in the anodic and cathodic processes, respectively.¹⁰⁵ The resulting DS-doped PPy cathode displayed the redox behavior of DS anions and PPy chains, affording a large reversible specific capacity of 115 mAh g⁻¹ at 50 mA g⁻¹ as a cathode in SIBs.

Water-soluble poly(2-methoxyaniline-5-sulfonic acid) (PMAS) has a free negatively charged sulfonate group per dimer unit, that can be incorporated into CP matrices as a dopant.¹⁰⁶ Yang *et al.* reported the Li storage properties of an electrochemically synthesized PMAS-doped PPy electrode.¹⁰⁷ PMAS as the supramolecular pre-order template can guide the growth of PPy resulting in the formation of a film with a very smooth surface other than the typical cauliflower morphology. PMAS showed its own redox activity in this composite, as revealed by the redox pairs (E/E' and P/P') when scanned over 2.0 - 4.0 V vs. Li/Li⁺. These peaks are related to the transition between different states of PMAS. Moreover, PMAS with such large molecular size was confined within the polymer matrix and became immobile, migration of smaller size cations (Li⁺) dominated in the charge/discharge process. The swelling and shrinking of PPy could be alleviated resulting in improved cycling stability. Benefiting from both the redox activity of PMAS and the intercalation/deintercalation of smaller size Li⁺, the resultant PPy/PMAS exhibited a greatly improved capacity of 120.6 mAh g⁻¹ at 0.1 A g⁻¹ as well as a high capacity retention rate of about 88.5% over 800 cycles at 1 A g⁻¹; in sharp contrast to the capacity of 81 mAh g⁻¹ and retention rate of 67.1% for PPy/pTS.

Various types of redox-active organic anions have been employed as dopants. Yoneyama *et al.* doped anthraquinone-1-sulfonate (AQS) ions into PPy films. The redox reactions of AQS generally involves an enolization reaction and a reverse reaction of carbonyl group: $\text{AQ-SO}_3^-/\text{AQ}^--\text{SO}_3^-$ and $\text{AQ}^--\text{SO}_3^-/\text{AQ}^{2-}-\text{SO}_3^-$, as evidenced by the additional redox peaks at -0.93 and -1.16 V vs. SCE in the cyclic voltammograms compared with PPy doped with sodium naphthalene-1-sulfonate (NtS). The AQS-doped PPy films showed a higher energy density of 150 mAh mL⁻¹, which is more than twice that delivered from PPy films doped with electrochemically inactive anions such as NtS or ClO₄⁻.¹⁰⁸ The incorporation of a second dopant, reduced graphene oxide (rGO), into PPy/AQS can further increase the charge storage by creating an interconnected porous structure. This structure was formed due to the overlapping of large graphene nanosheets that were used as templates and dopants during the growth of PPy.¹⁰⁹ This composite exhibited an improved capacity of 127.2 mAh g⁻¹ with ca. 100% coulombic efficiency at 0.1 A g⁻¹ over 500 cycles in a lithium battery. Such excellent performance is ascribed to the efficient pathway for ions and electrons transport within the porous structure. Lignosulfonate, a lignin derivative containing quinone groups, is a by-product of pulp and paper processing. It can be applied as dopant to be incorporated with PPy matrix. Quinone groups of lignosulfonate can be electrochemically reduced from its Q form (quinone) to its QH₂ form (phenol) along with the reduction of PPy (**Figure 5a**). Large amounts of quinone groups in this biopolymer effectively improved the charge storage by contributing an additional capacity of ~40 mAh g⁻¹ on top of PPy's 30-35 mAh g⁻¹ (**Figure 5b**).¹¹⁰ This work is of significance since it demonstrates the utilisation of industrial waste for fabricating battery electrode materials.

Redox-active molecules doped PANI has demonstrated improved electrochemical properties as well. Yamamoto and co-workers performed a systematic research on PANI integrated with redox-active dopants including ferrocene sulfonic acid (FcS), hydroquinone sulfonic acid (HQS), and naphthoquinone sulfonic acid (NQS).¹¹¹ Owing to their inherent redox activities, these dopants all contributed additional electrochemical performance to the composite. As a result, PANI doped with HQS and NQS respectively showed a higher capacity of 104 and 96 mAh g⁻¹ in the cell using zinc as an auxiliary electrode, while PANI doped with electrochemically inert ClO₄⁻ delivered a capacity of 84 mAh g⁻¹. PANI has also been applied as a cathode for aqueous rechargeable zinc-ion batteries with the combined Zn²⁺ insertion/extraction and dual-ion mechanisms.¹¹² Recently, Sun and co-workers reported the synthesis of sulfo self-doped PANI (PANI-S) nanorods with diameter and length of ~50 and

~200 nm, through a facile electrochemical copolymerization.¹¹³ As supported by the X-ray photoelectron spectroscopy characterization, PANI-S showed the ability to work as an organic reservoir to store multiple ions including the electrolyte species such as SO_4^{2-} and Zn^{2+} , as well as protons (H^+) (Figure 5c). Resulting from this unique mechanism, the PANI-S/Zn cell produced a capacity of 184 mAh g^{-1} at 0.2 A g^{-1} (Figure 5d). A high capacity of 110 mAh g^{-1} was still maintained at 10 A g^{-1} after 2,000 cycles. In contrast, the undoped PANI suffered from sharp capacity fading during the cycling.

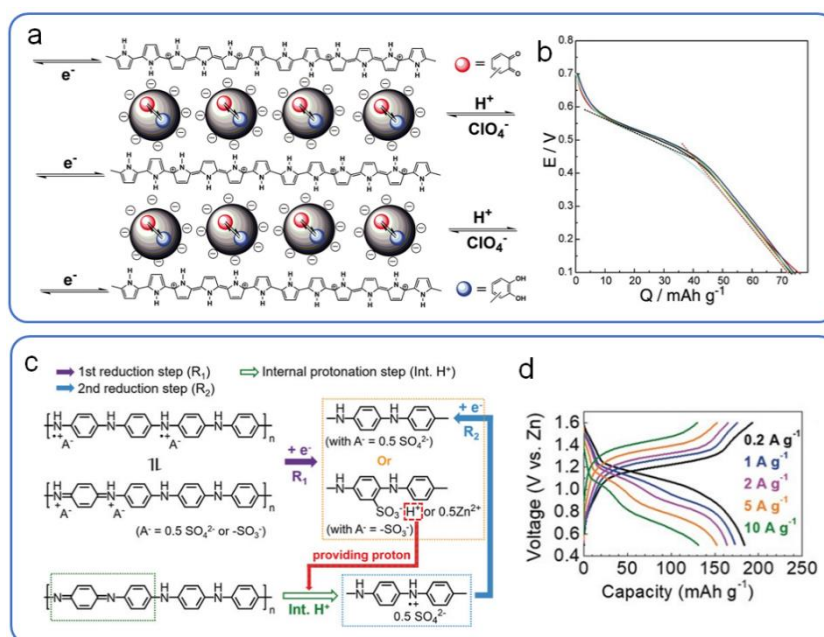
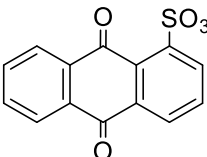
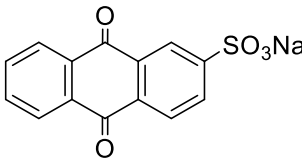
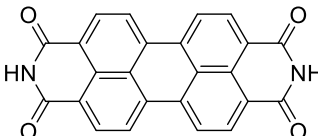
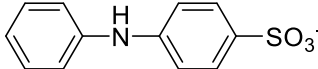


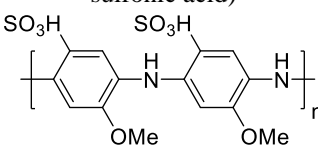
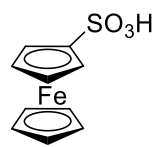
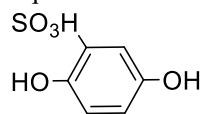
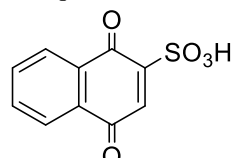
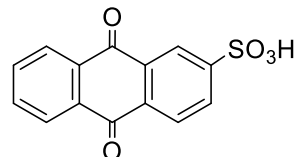
Figure 5 (a) The redox reaction of quinone functional groups in lignosulfonate within a PPy matrix; (b) Galvanostatic discharge curves of PPy/lignin film in 0.1 M HClO_4 at current densities from 0.83 to 16.7 A g^{-1} ; (Reproduced with permission from ref. 110. Copyright 2012, American Association for the Advancement of Science). (c) Proposed mechanism and structures of PANI-S upon charging (oxidation) and discharging (reduction) versus Zn metal; (d) Charge and discharge profiles of PANI-S/Zn cell at different current densities; (Reproduced with permission from ref. 113. Copyright 2018, Wiley-VCH Verlag GmbH & Co. KGaA.).

In summary, incorporating redox-active dopants into CPs has been demonstrated to be an effective approach for enhancing electrochemical performance. These dopants demonstrate their inherent electrochemical properties in addition to those from CPs. They contribute additional charge storage when applied in battery applications. Future work may focus on the development of new redox-active dopants and doping methods to achieve higher doping level

for enhanced redox capacity. An overview of this type of CPs and their energy storage properties are summarized in **Table 2**.

Table 2 Overview of Conducting Polymers Doped with Redox-Active Dopants for Secondary Batteries.

Back bone	Redox-active dopants	Cell type	Discharge capacity (mAh g ⁻¹)	Current density applied	Capacity loss (cycle no.)	Ref.
Polypyrrole	Potassium hexacyanoferrate <chem>K3Fe(CN)6</chem>	Li battery	69	C/30	Ascending tendency	101
	Sodium ferrocyanide <chem>Na4Fe(CN)6</chem>	Li battery	145	50 mA g ⁻¹	20% (100)	102
	Sodium ferrocyanide <chem>Na4Fe(CN)6</chem>	Na battery	135	50 mA g ⁻¹	15% (100)	103
	Anthraquinone-1-sulfonate 	vs. SCE	150 mAh mL ⁻¹	0.05 mA cm ⁻²	-	108
	Anthraquinone-2-sulfonate /graphene 	Li battery	127.2	0.1 A g ⁻¹	8.1% (500)	109
	Lignosulfonate	vs. Ag/AgCl	~75	0.83 A g ⁻¹	-	110
	Perylene-3,4,9,10-tetracarboxydiimide 	Li battery	>100	50 mA g ⁻¹	7.5% (190)	104
	Diphenylamine-4-sulfonate 	Na battery	115	50 mA g ⁻¹	18% (50)	105

Polyaniline	Poly(2-methoxyaniline-5-sulfonic acid) 	Li battery	120.6	0.1 A g ⁻¹	11.5% (800)	107
	Ferrocene sulfonic acid 		46			
	Hydroquinone sulfonic acid 		104			
	Naphthoquinone sulfonic acid 	vs. Zn		0.071 mA cm ⁻²	-	111
	Anthraquinone-2-benzoic acid 		64			

All-Polymer Batteries

Herein all-polymer batteries mean that cathode and anode electrodes are all based on CPs. They are free of metal-containing electrodes, thereby enabling a lightweight, flexible, environmentally benign and sustainable battery system. This system utilizes capacity-carrying polymeric materials as both anodes and cathodes, in which cations and/or anions move between electrodes in a rocking-chair motion to compensate the charge.¹¹⁴

n-Doped Conducting Polymer Electrode

In an ideal all-polymer battery, p-type polymer with higher redox potentials function as a cathode in combination with a n-type polymer anode.⁸¹ However, limited n-type CPs are available owing to their poor chemical stability and large impedance.¹¹⁵ In 1997, Searson *et al.* pioneered this field by coupling PTh electrodes bearing different fluorine-containing

aromatic rings with a polymer gel electrolyte.¹¹⁶ The maximum n-doping level of functional PTh was found to be correlated with the number of fluorine atoms on the phenyl ring. The assembled all-polymer dual-ion battery exhibited a discharge voltage of ~2.5 V and a capacity of 9.5-11.5 mAh g⁻¹ in the electrolyte of tetrabutylammonium tetrafluoroborate. Recently, several n-type conjugated redox polymers based on 5-alkyl-thieno[3,4-c]pyrrole-4,6-dione have been developed (**Figure 6a**).¹¹⁷ The effect of carbonyl group, alkyl chain and comonomer unit on the electrochemical activity of these polymers has been demonstrated. Incorporating an electron-withdrawing or electron-donating group with the conjugated backbone of polymer had a profound impact on its redox potential, which could vary over a range of 400 mV. The polymer with a redox potential of 1.55 V vs. Li/Li⁺ is suitable for application in a lithium-ion battery as an anode (Figure 6b).

Except those PThs, Jimenez *et al.* recently developed a lithium n-doped PANI for Li battery.¹¹⁸ Multiple redox states are involved in the protonation and deprotonation equilibrium of PANI, including the completely reduced leucoemeraldine base (LB), conducting emeraldine salt form (ES), and fully oxidized pernigraniline base (PNB).¹¹⁹ Research of PANI commonly centres on p-doped states (transitions from LB to ES, then ES to PNB) which involves simple acid-base reactions in water or protic media (Figure 6c). The deprotonation-induced n-doped of PANI needs cations, such as Na⁺ and K⁺, to compensate for the negatively charged nitrogen atoms.¹²⁰ Li-doped PANI (lithium emeraldinate) was prepared via a lithium-proton exchange on the emeraldine base (EB) in an anhydrous lithium-based electrolyte, since the EB form had distinct interaction with Li cations (Figure 7d). This lithium emeraldinate positive electrode can be discharged to 4.25 V vs. Li⁺/Li and displayed a coulombic efficiency of 99% after 400 cycles. The assembled cell delivered a specific capacity of 208 mAh g⁻¹ at 1/10 C, corresponding to 90.4% of its theoretical capacity. This lithium n-doped PANI shows the best performance in terms of high specific capacity and cycling stability in LIBs in this review.

Other conjugated polymers with homogeneous microporous structure have been used as a Li/Na n-doped electrode. A conjugated microporous polymer, 4,7-dicarbaryl-[2,1,3]-benzothiadiazole (PDCzBT), was synthesized via oxidative coupling polymerization.¹²¹ This polymer showed an ultrahigh specific surface area providing abundant active sites for storage. Uniform microporous structure is beneficial for the rapid transport of electrons and ions. A high discharge capacity of 1042 mAh g⁻¹ was delivered after 5 cycles, which may be ascribed to the mixed processes involving the Li doping and absorbing at the surface/interface.

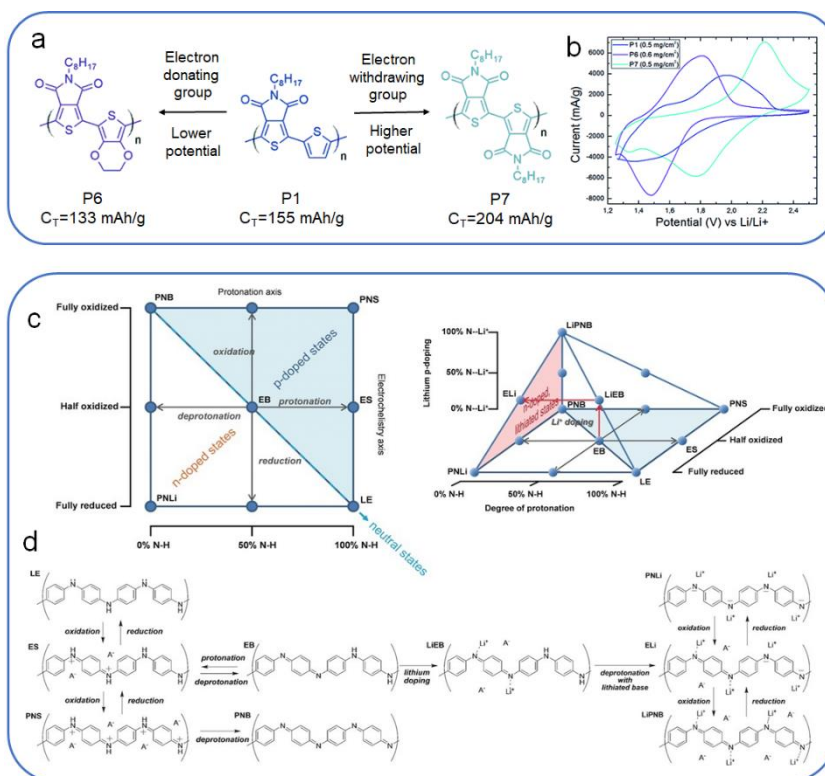


Figure 6 (a) Structure and theoretical capacities of n-type poly(5-alkyl-thieno[3,4-c]pyrrole-4,6-dione); (b) Cyclic voltammograms of n-type conjugated redox polymers; (Reproduced with permission from ref. 117. Copyright 2017, Royal Society of Chemistry). (c) Diagram showing the possible protonation and oxidation degrees of PANI and lithium n-doped states; (d) The formulae and reactions of PANI at different states, including the deprotonated-lithiated states (right); (Reproduced with permission from ref. 118. Copyright 2017, WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim).

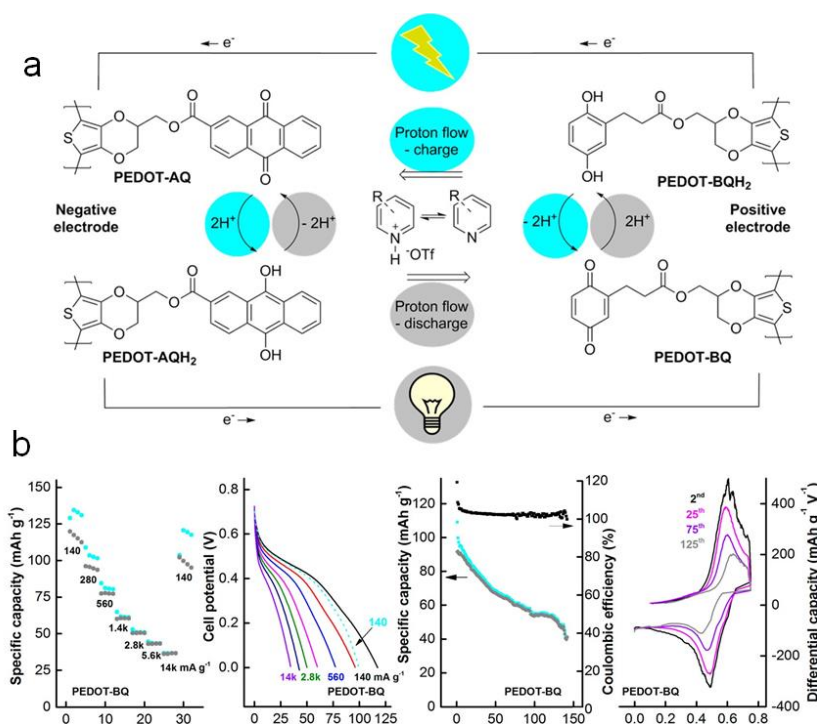
p-Doped Conducting Polymer Electrode

Currently the research on all-polymer batteries still mainly focus on using p-type CPs as both cathode and anode. An early attempt involved the use of PPy doped with large polymeric anion (polystyrenesulfonate, PSS) as a “pseudo n-dopable” anode.¹²² The charge compensation by cation (Li⁺) transport instead of PSS anions caused a negative shift in the oxidation potential, thus realized a voltage separation between PPy cathode at the reduced form and anode at the oxidized form. This system exhibited a specific charge capacity of 22 mAh g⁻¹, and no capacity loss over 100 cycles. Using PPy doped with different redox-active organic anions in an all-polymer battery system was demonstrated in 2006.¹²³ The dopants used for cathode and anode materials were indigo carmine (IC) and 2,2'-azino-bis(3-ethylbenzothiazoline-6-sulfonate) (ABTS), respectively. Both PPy/IC and PPy/ABTS exhibited large faradaic current response

over the applied potential range of -0.1 V to 0.8 V like neat dopants. The potential difference generated between these two redox reactions allowed them to perform as cathode and anode. The final full cell displayed a specific capacity of 15 mAh g⁻¹, which was equal to the estimated theoretical capacity. An all-polymer battery composed of free-standing electrodeposited PPy film electrodes has also been demonstrated, which provides a step forward towards the development of flexible all-polymer battery system.¹²⁴ PPy film doped with IC and *p*TS functioned as anode and cathode, respectively. This battery system displayed an initial discharge capacity of 21 mAh g⁻¹, a capacity retention rate of 76% over 50 cycles.

Like PPy, a potential difference can also be generated between the neutral state and an oxidized state (p-doped) for PEDOT, thus enabling the realisation of an all-polymer battery.¹²⁵ PEDOT has shown catalytic ability to oxygen reduction reaction.¹²⁶ Thus, a PEDOT-air battery was fabricated with polyethyleneimine (PEI) coated PEDOT/PSS anode and PEDOT/PSS cathode. During discharge, the PEI layer was consumed at the anode and O₂ was reduced at the PEDOT cathode, producing an open circuit voltage of about 0.5 V.¹²⁷ An optimized oxidation level of the PEDOT anode with a high electrical conductivity could be achieved by simply soaking it into mixtures of 1,8-diazabicyclo[5.4.0]undec-7-ene and dimethyl sulfoxide.¹²⁸ The assembled battery with a PEI-PEDOT/PSS anode and PEDOT/PSS cathode presented a discharge capacity of 0.02 mAh and an output power of 1.2 μW in the electrolyte of PSSNa.

Sjödin *et al.* recently demonstrated an all-polymer proton battery composed of PEDOT functionalized with anthraquinone (PEDOT-AQ) or benzoquinone (PEDOT-BQ) pendant groups as negative and positive electrode materials, respectively (**Figure 7a**).¹²⁹ The electrolyte containing proton donor and acceptor allowed the 2e⁻/2H⁺ quinone/hydroquinone redox reaction, and enabled the PEDOT backbone to be conductive in the potential region of quinone redox reaction. This all-polymer proton battery delivered a capacity of 120 mAh g⁻¹ with an average cell potential of 0.5 V based on PEDOT-BQ, 75% of its theoretical specific capacity (Figure 7b). They further developed two CRPs based on PEDOT with a hydroquinone pendant group.¹³⁰ The hydroquinone pendant group underwent stable proton cycling. These polymers showed fast redox conversion, making them suitable for aqueous rechargeable all-polymer battery.



Implantable medical devices (IMDs) have been widely used for therapies serving as functional devices to detect, prevent and cure diseases challenging human life.¹³³⁻¹³⁵ Currently, Li batteries are the predominant power sources to power IMDs since the first implantation of lithium iodine batteries for cardiac pacemakers in 1972.¹³⁶ Inevitably, Li batteries contain toxic chemicals which hamper their deployment with biomedical applications.¹³⁷ A bioelectric battery (bio-battery) with biocompatible electrodes that utilize body fluid as electrolyte is safe for implantation.¹³⁸ It is a type of metal-air battery that consists of a cathode for oxygen reduction reaction (ORR) and a sacrificial anode. The anode can be a biocompatible and bioresorbable metal, such as magnesium (Mg), zinc (Zn) and their alloys.¹³⁹

CPs with good electrical conductivity and electrocatalytic activity towards oxygen reduction have attracted attention as cathode materials in metal-air batteries.¹⁴⁰ In 2005, V. G. Khomenko *et al.* discussed the mechanism and feasibility of various types of CPs as ORR catalyst in acid and neutral electrolyte.^{141, 142} They proposed an “oxygen absorption” theory that molecular oxygen can be absorbed by the carbon atoms on the polymer chain to form an “oxygen-conductive polymer” bridging complex. This bridging complex could weaken the O-O bond of oxygen and lower the activation energy for reduction, leading to the electrocatalytic activity. In an Mg-air bio-battery, Mg anode is oxidized to Mg^{2+} and donates electrons when discharged; the CPs cathode, taking oxidized PPy as an example, takes up electrons and is reduced concomitantly and then the reduced PPy is re-oxidized (‘recharged’) by oxygen as illustrated in **Figure 8**.¹⁴³ The ORR mechanism in PEDOT has also been revealed using the density functional theory.¹⁴¹ Its catalytic activity is proposed to be related to the formation of polaronic states, which leads to the decreased HOMO-LUMO gap and an enhanced reactivity. In a recent study, the doping of polymer by oxygen during ORR was convinced by decoupling the conductivity (intrinsic property) from electrocatalysis (an extrinsic phenomenon).¹⁴⁴ Hence, the PEDOT electrode is electrochemically reduced (undoped) in the voltage range of ORR regime, but O_2 keeps it conducting; ensuring PEDOT to act as an electrode for the ORR.

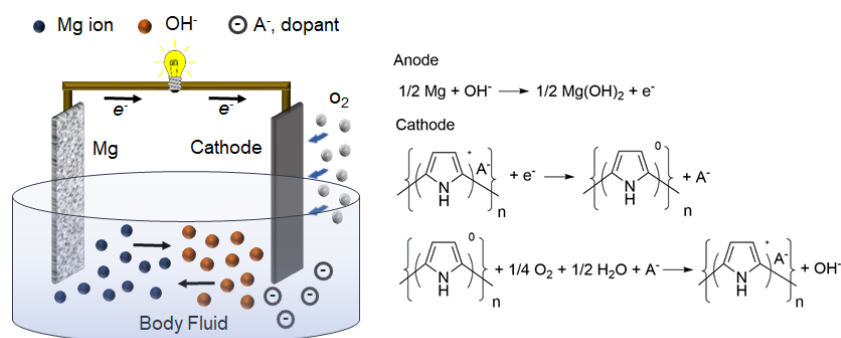


Figure 8 Schematic working principle and general redox chemistries of a Mg-air bio-battery using PPy cathode when being discharged (A^- represents mobile charge balance anions).

Cytocompatible Conducting Polymer Electrodes

Electrodes should be cyto- and tissue-compatible for applications in bio-batteries. CPs, particularly PPy and PEDOT, are biocompatible with various cell types and tissues and have been thoroughly evaluated as biomaterials both *in vitro* and *in vivo*.¹⁴⁵ They have demonstrated excellent cytocompatibility for supporting the *in-vitro* adhesion, growth and differentiation of a wide range of cell types such as bone, neural, glial, rat pheochromocytoma and endothelial cells, fibroblasts, keratinocytes and mesenchymal stem cells.¹⁴⁶ PPy also showed good tissue-compatibility in animal models with no significant long-term adverse effect *in vivo* or inducing only a minimal tissue response.¹⁴⁷ It should be pointed out that the cytocompatibility of CPs depends on their surface charge, surface properties (i.e., roughness, morphology, wettability), and stiffness as well; all these are closely related with the polymerization methods and conditions used.¹⁴⁸ The cytocompatibility can be improved by removing the impurities such as unused reactants and monomers as well as the produced short oligomers. Additionally, the integration with bioactive molecules (*e.g.*, polysaccharides, proteins, and even whole living cells) can further modulate the biological functionality of CPs, which can be achieved by physical approach (entrapping, blending) and chemical approach (doping, covalent attaching).¹⁴⁹ Dopants form a major constituent of a CP, and hence affect its inherent chemical-biological properties. PPy doped with different biomolecules have demonstrated efficacy for biomedical applications, such as dermatan sulphate for increasing keratinocyte viability, heparin for increasing the proliferation of endothelial cells, and laminin-derived peptides to control neuron and astrocyte adhesion.^{150, 151}

PPy cathode (doped with a biomolecule, dextran sulfate) coupled with a bioresorbable Mg alloy anode could maintain a cell voltage of about 1.4 V for 19 h at a current density of 30 mA g⁻¹ in phosphate buffered saline (PBS) electrolyte.¹⁵² Incorporating a biocompatible dopant with an electrocatalytic ability to ORR can further improve the performance. The molecule AQS with ORR capability was co-doped with reduced graphene oxide (r-GO) into PPy matrix.¹⁵³ The formed PPy/AQS/r-GO composite delivered a maximum power density of 6240.5 mW m⁻² in PBS, 14.2 times higher than that of PPy/pTS. The mechanical properties of CPs can also be manipulated to match that of body tissue (2-30 kPa). A two components conducting polymer-based hydrogel was developed via electrodepositing PPy onto an ionically crosslinked PEDOT

hydrogel with Mg^{2+} (**Figure 9a**).¹⁵⁴ It demonstrated the joint merits of conductivity and electroactivity of CPs and “soft nature” of a hydrogel, making it a versatile platform for tissue engineering and energy storage applications (Figure 9b). This cytocompatible PPy/PEDOT hydrogel coupled with an Mg anode provided a stable voltage of 0.7 V for about 160 h at a current density of $200 \mu\text{A cm}^{-2}$, affording a capacity of 32 mAh cm^{-2} and an energy density of 22 mWh cm^{-2} in PBS electrolyte (Figure 9c).

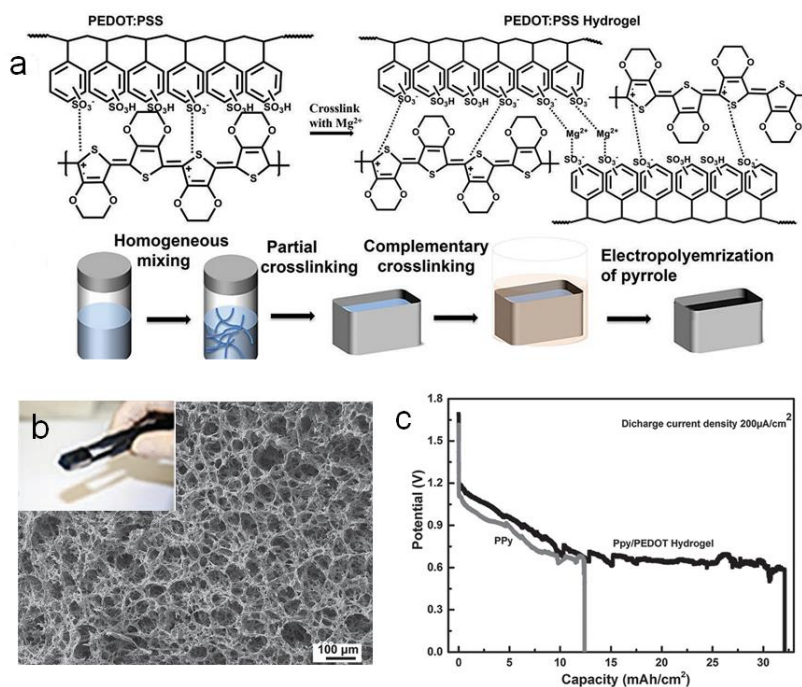


Figure 9 (a) Crosslinking process of PEDOT-PSS hydrogel and schematic procedures to fabricate PEDOT hydrogel and PPy/PEDOT hydrogel; (b) Cross-sectional and digital (inset) images of PPy/PEDOT hydrogel; (c) Discharge curves of a Mg bio-battery with a PPy/PEDOT hydrogel or a PPy cathode at $200 \mu\text{A cm}^{-2}$ in PBS; (Reproduced with permission from ref. 154. Copyright 2016, WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim).

Biodegradable Conducting Polymer Electrodes

A biodegradable battery system is an ideal choice to provide the energy for the emerging transient implants.^{155, 156} They facilitate biological processes that enable/facilitate repair of damaged tissue by supporting biological processes in a controlled fashion.^{157, 158} However, CPs are stable under physiological conditions and, therefore, they need to be modified to attain biodegradability.¹⁵⁹

An important approach is to synthesize a block copolymer that contains conjugated oligomers and degradable subunits. As model compounds of CPs, conjugated oligomers with well-defined structures have been heavily investigated due to their good electroactivity, enhanced solubility and excellent processability.¹⁶⁰ Moreover, oligomers of CPs can be consumed by macrophages, and subsequently cleared by kidney.^{161, 162} To achieve optimal mechanical, electrical and biological properties and degradation profile for a targeted application, it is desirable to promote architectural diversity (*e.g.*, linear, grafted, star-shaped, hyperbranched, crosslinked).^{163, 164} Schmidt's group have synthesized a series of biodegradable and conductive block copolymers composed of degradable ester linkers and conjugated oligomers, including oligopyrroles, oligothiophenes and oligoanilines.^{165, 166} However, the electronic conductivity is impeded by the limited availability of dopants and low extent of π -conjugation along the polymer backbone, thus not suitable for battery applications.

Synthesizing conducting polymer composites or blends with a biodegradable polymer is another important strategy to fabricate biodegradable conductive polymers. These composites/blends are usually prepared by emulsion polymerization of conducting polymer nanoparticles in the synthetic polymer solution, followed by precipitation with organic solvents and a wash with deionized water.¹⁶⁷ They can be further processed into a membrane by casting onto a plate. The conductivity and biodegradability can be controlled by adjusting the proportions of conducting polymer in the blend/composite. However, CPs nanoparticles at low content are unable to form a conductive network within the biodegradable polymer matrix. Generally, these biodegradable conductive copolymers or composites/blends usually suffer from a low conductivity (10^{-7} - 10^{-3} S cm⁻¹) and poor electrochemical activity, making them unsuitable for battery applications.¹⁶⁸

To achieve a high conductivity and electrocatalytic activity while ensuring a large biodegradability, a bilayer structure for combining two components is an option.¹⁶⁹ Jia *et al.* demonstrated a novel air cathode material by chemically depositing a thin continuous PPy layer only onto one side of a silk film (SF-PPy).¹⁷⁰ This bilayer structure facilitated the enzyme to attack the silk film with cleavage sites available on the opposite side. This film showed a conductivity of ~ 1.1 S cm⁻¹. It degraded in a concentrated buffered protease XIV solution, with a weight loss of 82% after 15 days (**Figure 10a**). Degradation of the silk substrate led to fracture and disintegration of SF-PPy film (**Figure 10b**), thereby offering the possibility of elimination by renal excretion, phagocytosis, and/or endocytosis. The assembled Mg-air bio-battery

exhibited a discharge capacity of up to 3.79 mAh cm^{-2} at a current of $10 \mu\text{A cm}^{-2}$, offering a specific energy density of $\sim 4.70 \text{ mW h cm}^{-2}$ (Figure 10c).

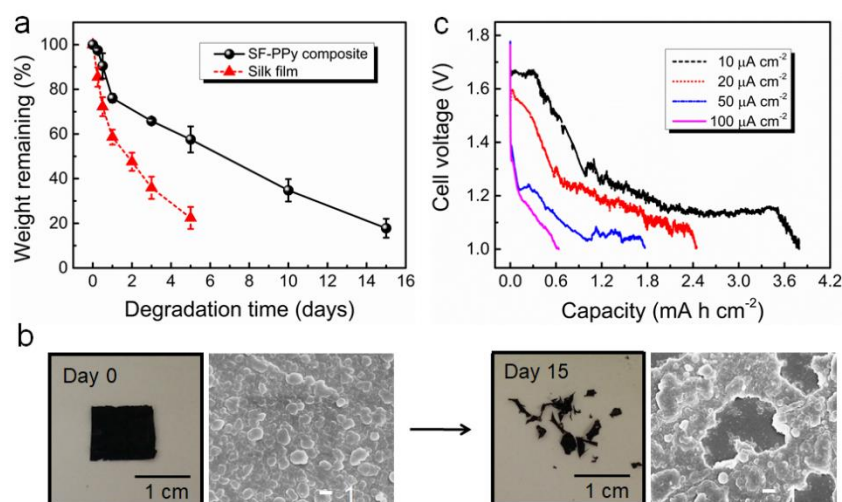


Figure 10 (a) Quantitative changes of silk film and SF-PPy film cultivated in buffered 1.0 mg mL^{-1} protease XIV solution; (b) Optical and SEM images of SF-PPy film before and after biodegradation; (c) Galvanostatical discharge curves of a Mg-air bio-battery composed of SF-PPy film at various current densities in PBS electrolyte; (Reproduced with permission from ref. 170. Copyright 2016, WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim).

Engineering Solution Processability of Conducting Polymers

Creating diverse energy storage devices with customized structures and configurations necessitates the continued development of materials processing and fabrication methods.¹⁷¹ Advanced fiber-spinning and 3D printing techniques are tools that enable engineering unconventional configurations, such as fiber-shaped or patterned micro-dimensional electrodes.¹⁷² These electrodes in novel form can be seamlessly integrated into unconventional battery architectures being a structural component of functional devices.^{173,160} Fiber-shaped electrodes have omnidirectional flexibility and can be integrated into smart textiles.¹⁷⁴ Three-dimensional micro-scaled electrodes are essential to achieve miniaturized batteries with high performance.¹⁷⁵ Beyond that, CPs can also be processed into mechanically robust, free-standing films. This allows for easy fabrication of thin flexible/wearable batteries that can be bent, folded or even stretched while maintaining their functional properties. This type of electrode offer advantages of high energy density and long cycle life by avoiding the drawbacks

of dead weight/volume of additives and enhanced mechanical stability during charge-discharge cycling.¹⁷⁶⁻¹⁷⁸

Although CPs are of intrinsic flexibility, they typically lack solution processability due to the rigid conjugated main chain. CPs can be readily tailored by modifying the molecular structure to enable the solution processability. Fabricating hydrophilic CPs nanoparticles is attractive regarding the processing in water-based solvents. Attaching appropriate flexible side chains (substituents) can make CPs soluble in organic solvents, for example, P3HT is soluble in organic solvents such as toluene, chlorobenzene and dichlorobenzene.¹⁷⁹ A water-soluble self-doped PANI, poly(2-methoxyaniline-5-sulfonate), was synthesised by chemical and electrochemical polymerization via introducing sulfonic acid groups onto the polymer backbone.¹⁸⁰ Cao *et al.* synthesized soluble PANI by using a functionalized protonic acid to protonate PANI.^{181, 182} The counterion, dodecylbenzenesulphonic acid (DBSA), can endow processability of PANI at the emeraldine base form with a high conductivity of 10^2 S cm^{-1} .

Spinnable Conducting Polymers Fiber

Flexible fiber-type batteries are lightweight, easily folded, woven into textiles or even reshaped into other architectures with high efficiency at low cost.¹⁷³ Fiber electrodes can be arranged either helically or in parallel for constructing batteries. Among all fiber spinning methods, wet spinning is the most used to produce CPs fibers owing to its ease of processing (**Figure 11a**).¹⁸³ CPs dispersed in a solvent are extruded into a coagulation bath in which fibers are solidified. PANI was the first wet-spinning produced fiber, as its emeraldine form was soluble in N-methyl-2-pyrrolidinone (NMP) or N,N'-dimethyl propylene urea (DMPU) to form the spinning solution.¹⁸⁴ This facile fabrication technique can produce fibers of long length with a large aspect ratio and high alignment. The PANI fiber with a conductivity of 140 S cm^{-1} and a tensile strength in the order of 3-4 GPa have been produced. With a CNT content of 0.25 wt%, it exhibited a discharge capacity of 12.1 mAh g^{-1} when tested in an ionic liquid electrolyte, ethylmethyl-bis-(trifluoromethane sulfonyl) amide (EMI.TFSA) (**Figure 11b,c**).¹⁸⁵ PEDOT-PSS fibers can also be fabricated via wet-spinning from an aqueous colloidal suspension with a diameter ranging between 4.6-16 μm with a conductivity of $\sim 0.1 \text{ S cm}^{-1}$.¹⁸⁶

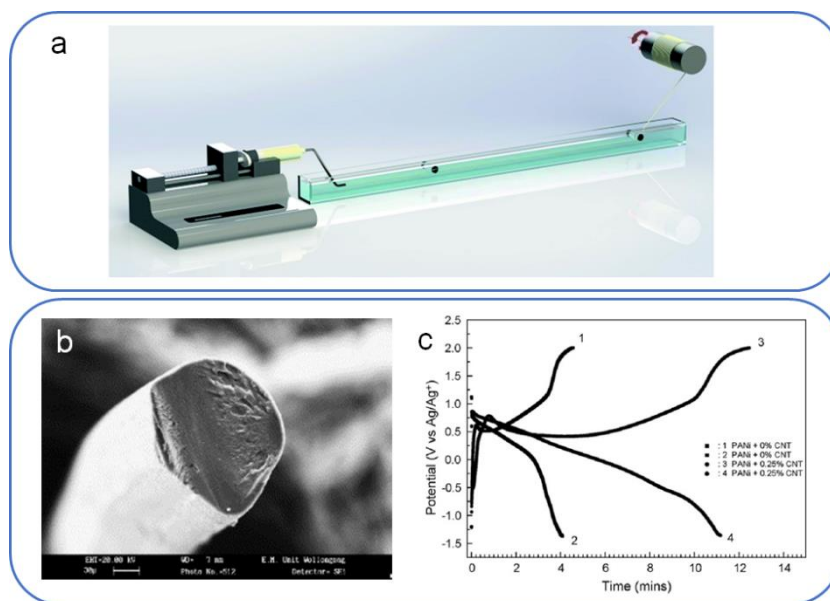


Figure 11 (a) Schematic of a wet spinning process; (Reproduced with permission from ref. 183. Copyright 2016, Royal Society of Chemistry). (b) Scanning electron micrographs of PANI/CNT fiber electrode; (c) Charge and discharge of PANI fiber (1 and 2) and PANI/CNT fiber (3 and 4) in EMI.TFSA; (Reproduced with permission from ref. 185. Copyright 2007, Elsevier Ltd).

Unlike wet spinning producing microfibers, electrospinning is a versatile method to produce polymer fibers at the nano- to submicron scale.¹⁸⁷ Electrospun nanofibers show unique properties including nanointerface, high surface-to-volume ratio, and large surface area; they are all the factors to improve the performance of energy storage devices.¹⁸⁸ During the electrospinning processes, polymer solution is extruded from an orifice to form a small droplet in the presence of an electric field and then extruded from the cone, resulting in the formation of micro/nanofiber. Pure PANI nanofibers with diameters of hundreds nanometres were produced via electrospinning without adding non-conductive polymers.¹⁸⁹ Electrospun PPy/sulfonated-poly(styrene-ethylene-butylene-styrene) composite nanofibers with a diameter of 300 nm were prepared.¹⁹⁰ This material delivered a discharge capacity of 80 mAh g⁻¹ coupled with a Li metal anode, higher than that 48 mAh g⁻¹ from traditional casting fibers.

Printable Conducting Polymer Electrode

Printable power sources can be fully integrated with printed electronics. Printing is a versatile fabrication method for creating free-form two- and three-dimensional structures. It has emerged as a powerful tool for fabricating micro-dimensional electrodes with pre-designed

patterns.¹⁹¹ Among various printing technologies, screen printing and inkjet printing are preferred because they are amenable to large-scale production.¹⁹² Screen printing is a simple and environmentally friendly way to produce electronic circuitry and make interconnections, while inkjet printing has emerged as an attractive patterning technique due to its high resolution.¹⁹³ Beyond those, direct ink writing, a 3D printing technology, enables almost infinite possibilities for controllable 3D structural prototyping.¹⁹⁴ Printing technologies rely heavily on the properties of inks. The key challenge to achieve printable CPs exists in the ink formulations, which should provide appropriate delivery and curing characteristics while preserving high conductivity. Colloidal particles serve as a role equivalent to pigments in an ink solution and are critical for processing CPs.

Nanodispersions of CPs can be formed with the sterically stabilized colloids that consist of an inner core of CPs nanoparticles surrounded by an outer layer of absorbed, insulating stabilizer.¹⁹⁵ Polyvinyl alcohol, polyvinyl pyrrolidone, and polyethylene oxide are the frequently used stabilizers. Poly(vinyl alcohol-co-acetate) stabilized PPy dispersion has been produced, and the subsequent PPy film on gold layer fabricated by printing has been demonstrated.¹⁹⁶ Aqueous PANI nanodispersion doped with DBSA with a uniform particle size of 80 nm is suitable for use as inks, as demonstrated by the high-quality patterns on paper in just 30 s via inkjet printing.¹⁹⁷ Colloidal dispersions of CPs can also be prepared in micellar solution via micro-emulsion polymerization, in which particle size is predetermined by the micelle template. PEDOT nanoparticles with a size over a range of 30-100 nm and a conductivity of 50 S cm^{-1} was obtained via such polymerization.¹⁹⁸ High-resolution 3D PANI structures were fabricated by direct ink writing method, where the processability of PANI/DBSA was achieved by means of a counterion induced thermal doping method.¹⁹⁹

The use of printed CPs currently has centred on the creation of chemosensors, biosensors, solar cells, and consumer electronics.^{200, 201} Flexible patterned supercapacitors composed of PANI or PEDOT electrode have been achieved through screen printing and inkjet printing.^{202, 203} Printing techniques normally produce a thin-film electrode, leading to a high gravimetric capacity. Clark *et al.* firstly demonstrated a flexible zinc-air battery on paper with a screen-printed zinc/carbon/polymer composite anode.²⁰⁴ The PEDOT cathode was prepared by inkjet printing oxidant solution in patterns onto paper, followed by vapour phase polymerisation of the monomer. This paper-based battery exhibited a discharge capacity of 0.5 mAh cm^{-2} with an open-circuit voltage of 1.2 V. An ultra-thin all-polymer battery has been assembled from

bipolar PEDOT-PSS electrodes (same material in the cathode and anode) on polyethyleneimine (PEI) film via screen printing technology (**Figure 12a,b**).²⁰⁵ The difference in the oxidation level between these two electrodes produced an open circuit voltage of 0.60 V and displayed a specific capacity of 5.5 mAh g⁻¹ (Figure 12c).

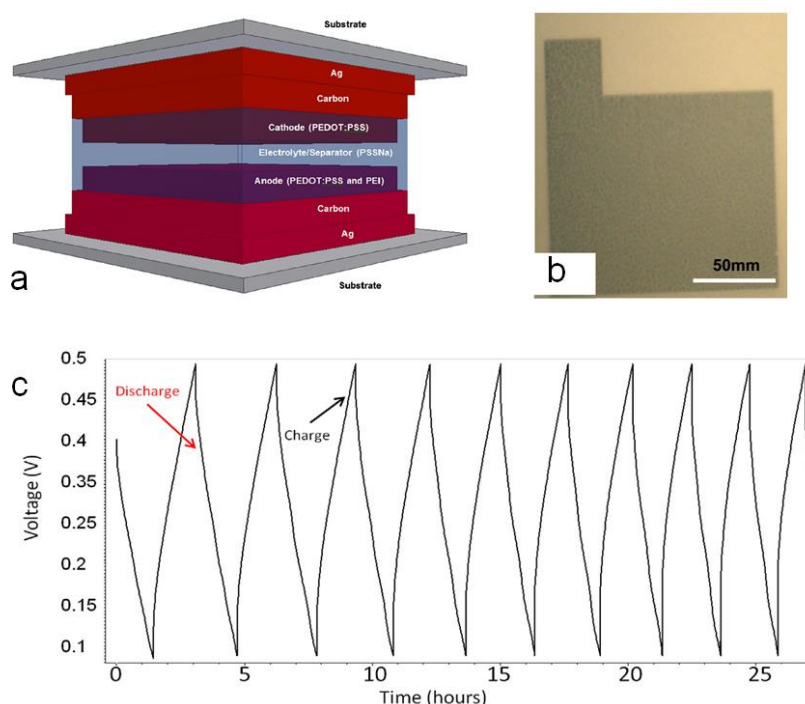


Figure 12 (a) Schematic diagram of a printed polymer battery; (b) Micrographs of PEDOT-PEI electrode; (c) Charge and discharge curves of a bipolar polymer battery composed of PEDOT-PSS electrodes at a current of 0.6 μ A; (Reproduced with permission from ref. 205. Copyright 2015, Elsevier Ltd).

Conclusions and Outlook

Research on energy storage is driven by the huge electronic devices market. CPs are promising energy storage materials due to their sustainability, light weight, ease of processability and tailorable electrochemical properties. Their relatively low specific capacities resulting from the low doping level have not been an obstacle to their development.

Through chemical modification of CP backbone with pendant redox-active groups or inserted as counterion dopants, additional redox active sites are introduced resulting in improved electrochemical performance. The vast toolbox of organic chemistry enables facile chemical engineering of molecular structure. For designing these conducting redox polymers, proper

selection of redox group and backbone types needs to be considered to achieve a potential match. Redox reactions of pendant groups need to occur within the potential region defined by the CP backbone to ensure that the polymer chain is conductive and electrochemically stable. This is the prerequisite to achieve fast charge transfer, stable redox cycling and simultaneously avoiding charge capacity losses due to inactive (resistive) regions. An appropriate choice of a linker between redox group and backbone is another critically important aspect to preserve the individual redox behavior of active moieties. The bridge connecting pendants and polymer chain has a great impact on the electrochemical properties of substituted materials by modulating the interaction between polymer backbone and redox pendants.

Another critical factor that determines the conductivity and capacity of CPs is precise manipulation of doping. The realisation of stable n-doped CPs with high charge storage determines the development of all-polymer battery when coupled with a p-doped CP. The doping mechanism of inserting metal cations onto the atoms with lone pair electrons (O, N) and unsaturated carbon atoms may offer new opportunities as anodes. In a rechargeable battery, dopants forms a major constituent for the electrolyte. It is highly recommended to choose a proper dopant that shows a high ionic mobility and a good ion-solvent interaction with CPs.

Cycling stability is also an important issue facing the application of organic electrodes in rechargeable batteries. Pristine CPs commonly suffer from poor cycling stability due to the degradation induced by volume changes during the charge/discharge cycling, as well as the inactive structural changes stemmed from the irreversible overoxidation reaction at high voltage. To overcome these problems, two approaches may be applied: the incorporation of immobilised dopants such as large sheet rGO that allows the insertion of small ions for alleviating volume changes; the introduction of electron-rich fused rings into the conjugated backbone to improve the stability of conjugated polymers at high voltages.

Recent research not only focuses on enhancing the battery performance but also shifting towards additional functionalities and unconventional architectures. New functionality, such as biodegradability, could be endowed when incorporating chemically degradable units into the backbone of CPs or forming biopolymer-CP composites/blends. This design could obviate the need to regulate molecular weight as the polymer would be hydrolytically and/or enzymatically degraded *in vivo*, generating polymer fragments that would be small enough to be renally cleared. The versatility afforded on functionalizing CPs opens the door for more advanced applications in implantable medical devices.

Developing stable solutions or colloidal dispersions of CPs is crucial for subsequent processing. Solubility of CPs can be controlled by grafting pendant groups to the backbone. CPs electrodes in unconventional configurations hold great promise in the seamless integration of batteries with wearable or implantable electronic devices. Another emerging research trend in the battery industry is miniaturization retaining high performance. The development of micro-scaled energy storage devices is critical to the development of autonomous electronic systems and wireless technologies. Low-cost printing techniques can significantly contribute micro-sized electrodes and batteries based on CPs.

The diversity in molecular structure attainable through synthetic strategies currently available enables precise tuning of CPs that can promote the development of sustainable and versatile energy storage systems. A thorough understanding of the redox processes as well as the structural changes of CPs occurring within a battery system using *in situ/operando* characterization techniques will provide further information to enable the design and synthesis of new CPs.

Conflicts of interest

There are no conflicts to declare.

Acknowledgement

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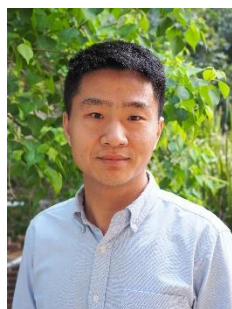
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Author introduction



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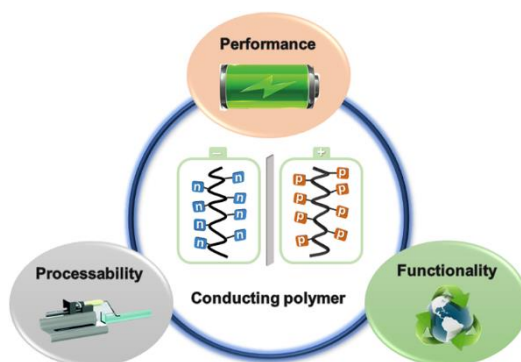
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Conducting polymers with structural diversity in molecular design has enabled the modulation of their intrinsic properties towards sustainable and versatile batteries.



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